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Volatile Organic Compound Emissions from 46 In-Use Passenger Cars

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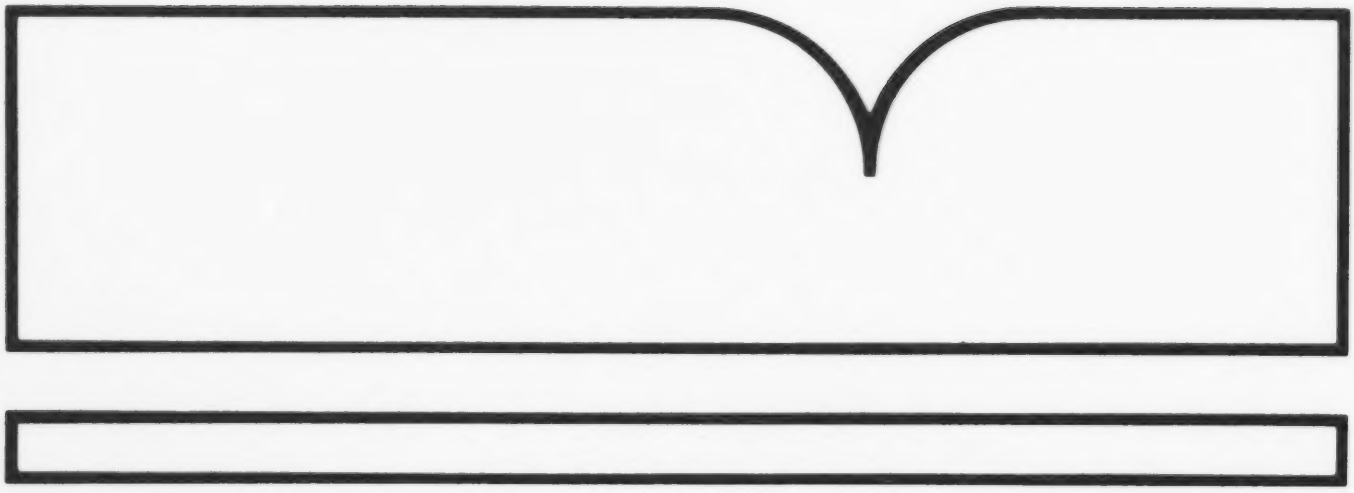

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16. ABSTRACT

Emissions from automobiles have long been considered a prime source of pollutants involved in smog formation and ozone production. The reactive potential of the species emitted has been studied extensively, and many reactivity schemes have been proposed. Most of the data on the detailed composition of the emissions from automobiles were taken from new or prototype vehicles. This study was undertaken to ascertain the mass and the detailed hydrocarbon and aldehyde composition of emissions from vehicles actually driven by the public. Forty-six vehicles, 1975 through 1982 models, were tested by using the Federal Test Procedure driving cycle, the Hot Soak Evaporative Test, the New York City driving cycle, and the Crowded Urban Expressway driving cycle, also known as the Sulfate Cycle. Overall composition was quite consistent among cycles and years, with some changes occurring in the 1981 and 1982 models. Mass emissions decreased with model year, showing the most significant decreases in latter years as the standards became more stringent. Eighty-two individual hydrocarbons and 10 aldehydes are reported for each test condition. The ratio of hydrocarbons to oxides of nitrogen increased dramatically on the lower speed cycles.

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Volatile Organic Compound Emissions from 46 In-Use Passenger Cars

John E. Sigsby, Jr.,* Silvestre Tejada, and William Ray

Mobile Sources Emission Research Branch, Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27710

John M. Lang and John W. Duncan

Northrop Services, Inc., Research Triangle Park, North Carolina 27709

■ Emissions from automobiles have long been considered a prime source of pollutants involved in smog formation and ozone production. The reactive potential of the species emitted has been studied extensively, and many reactivity schemes have been proposed. Most of the data on the detailed composition of the emissions from automobiles were taken from new or prototype vehicles. This study was undertaken to ascertain the mass and the detailed hydrocarbon and aldehyde composition of emissions from vehicles actually driven by the public. A total of 46 vehicles, 1975–1982 models, were tested by the federal test procedure driving cycle, the hot soak evaporative test, the New York City driving cycle, and the crowded urban expressway driving cycle, also known as the sulfate cycle. Overall composition was quite consistent among cycles and years, with some changes occurring in the 1981 and 1982 models. Mass emissions decreased with model year, showing the most significant decreases in latter years as the standards became more stringent. A total of 82 individual hydrocarbons and 10 aldehydes are reported for each test condition. The ratio of hydrocarbons to oxides of nitrogen increased dramatically on the lower speed cycles.

Introduction

Automotive emissions have been related to photochemical smog and ozone formation for many years. The impact of automobile exhaust on smog formation is related to the internal composition of the exhaust gas. Reactivity schemes have been generated by almost all parties interested in the subject. The basic information was applied to atmospheric models that currently are becoming sophisticated enough to handle compositional variations (*1–3*). Input to all of these schemes requires detailed compositional data on automobile exhaust. Little has been published recently; detailed hydrocarbon composition was last described in 1977 by Black and High (*4*), again in 1980 (*5*), and in 1978 by Jackson (*6*). There are very little data on aldehydes (*7–9*). All of the vehicles in these previous programs were either new or at least "well-tuned" to manufacturers specifications. Many of the studies were on "prototype" emissions control systems. Little is known of the composition of emissions from production vehicles or those used by the general public.

Most of the previous work used only the federal test procedure (FTP) cycle to simulate emissions. This is a typical urban driving pattern as would have been seen in Los Angeles in the late 1960s. It is not typical of center-city driving, as in New York City, or of high-speed conditions.

This program was designed to investigate the detailed emissions, including aldehydes, from emission-controlled vehicles made in 1975 and later. Almost all were catalytically controlled and reflect the systems designed to meet the varying standards of each model year. An attempt to remove fuel variability was made, and except for the first six cars, a single fuel was used throughout the program. Emissions were measured with three well-known driving cycles: the FTP, the crowded urban expressway (CUE or S7), and the New York City cycle (NYCC). Due to difficulties in instrumenting fuel tanks, the diurnal evaporative emissions test was not run, but the hot soak portion of the FTP was included in order to provide an estimate of evaporative emissions.

Experimental Section

Vehicles Tested. The vehicles tested were desired to be representative of in-use vehicles with 49 state emission control devices produced after 1974. The desired mix was determined from sales figures from 1975 to 1982 and registration predictions from Mobile 2. This mix is shown in Table I along with the number actually tested. Vehicles were acquired from the general public by advertising locally and by offering an incentive and a loaner vehicle while the vehicle was tested. From the responses, vehicles were selected to match the desired distribution as closely as possible. Vehicle availability and specific interest led to a slightly larger proportion of 1981 vehicles than was initially determined. In each manufacturer–year category, efforts were made to provide as much variation as possible. Overall, the match between planned and tested distribution was very close. A detailed description of each of the 46 vehicles and their control systems is given in the supplementary material (see paragraph at end of paper regarding supplementary material). Each car is numbered and described by year, make, model, engine displacement, number of cylinders, carburetor, and control devices.

Fuel Used. Two commercial fuels were used in this program. Fuel inspection results and detailed hydrocarbon distribution are shown in Table II. The two fuels were quite different; one was a summer-grade (volatility class A) premium fuel, and the other was a winter-grade (volatility class D) regular-grade fuel. The volatility difference was primarily seen as an increase in the butanes of from

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Table I. VOC Test Fleet (80% U.S.–20% Import) Percentage in Each Category, Goal (Actual)

	model year							
	1975	1976	1977	1978	1979	1980	1981	1982
percent	8 (6)	12 (9)	13 (9)	10 (11)	12 (11)	15 (15)	17 (26)	13 (13)
GM	2 (1)	2 (2)	3 (2)	2 (1)	2 (1)	3 (3)	4 (6)	3 (3)
Ford	1 (1)	1 (1)	1 (0)	1 (2)	1 (1)	1 (1)	2 (3)	1 (1)
Chrysler	0 (1)	1 (0)	1 (0)	1 (1)	1 (1)	1 (1)	0 (0)	1 (1)
AMC	1 (0)	1 (0)	0 (1)	0 (0)	0 (0)	0 (0)	0 (1)	0 (0)
imports	0 (0)	1 (1)	1 (1)	1 (1)	2 (2)	2 (2)	2 (2)	1 (1)
total	4 (3)	6 (4)	6 (4)	5 (5)	6 (5)	7 (7)	8 (12)	6 (6)

Table II. Fuels Used and Detailed Hydrocarbon Percent Composition

	76 no-lead regular	Amoco premium no lead		76 no-lead regular	Amoco premium no lead
percent evaporated at 65 °C	26.7	22.5	octane index	87.1	92.9
percent evaporated at 118 °C	62.7	65.5	vapor pressure	12.2	8.8
percent evaporated at 190 °C	94.7	98.0	sulphur, wt %	0.034	0.021
end point, °C	215	195	API gravity at 60 °F	61.05	53.60

		percent composition				percent composition	
no.	hydrocarbon[a]	76 no-lead regular	Amoco premium no lead	no.	hydrocarbon[a]	76 no-lead regular	Amoco premium no lead
8	isobutane	1.86	1.40	47	2-methylheptane/1-methylcyclohexene	0.37	0.10
9	1-butene/isobutylene	0.00	0.00	48	4-methylheptane	1.20	0.25
10	*n*-butane/1,3-butadiene	7.75	3.52	49	3-methylheptane	0.70	0.23
11	*trans*-2-butene/2,2-dimethylpropane	0.25	0.13	50	2,2,5-trimethylhexane	0.81	0.76
12	*cis*-2-butene/1-butyne	0.25	0.13	51	*n*-octane	0.76	0.20
13	3-methyl-1-butene	0.10	0.07	52	2,3,5-trimethylhexane	0.18	0.13
14	isopentane	6.16	7.12	53	2,4-dmethylheptane	0.14	0.08
15	1-pentene/2-butyne	0.32	0.18	54	2,5- and 3,5-dimethylheptane	0.24	0.09
16	*n*-pentane	3.06	2.37	55	ethylbenzene/2,3-dimethylheptane	1.17	0.94
17	2-methyl-1,3-butadiene	0.00	0.00	56	*p*- and *m*-xylene	4.58	2.60
18	*trans*-2-pentene	0.89	0.73	57	2-methyloctane	0.00	0.00
19	*cis*-2-pentene	0.51	0.41	58	2,4,5-trimethylheptane	0.37	0.10
20	2-methyl-2-butene	1.22	1.50	59	*o*-xylene/unknown C_9 paraffin	2.46	1.61
21	2,2-dimethylbutane	0.41	0.08	60	2,4-dimethyloctane	0.14	0.05
22	cyclopentene	0.37	0.31	61	*n*-nonane	0.27	0.18
23	cyclopentane/3- and 4-methyl-1-pentene	0.48	0.42	62	C_{10} paraffin	0.16	0.32
24	2,3-dimethylbutane	0.86	0.78	63	*n*-propylbenzene	0.70	0.90
25	2-methylpentane/2,3-dimethyl-1-butene	2.76	2.76	64	1,3,5-trimethylbenzene	2.74	3.35
26	3-methylpentane	1.76	1.47	65	3,4-dimethyloctane	1.12	1.42
27	1-hexene/2-ethyl-1-butene	0.64	0.64	66	1-methyl-3-ethylbenzene	1.52	1.53
28	*n*-hexane/*cis*-3-hexene	1.32	0.83	67	1-methyl-2-ethylbenzene	0.28	0.07
29	*trans*-3-hexene	0.80	0.73	68	1,2,4-trimethylbenzene	3.75	4.59
30	2-methyl-2-pentene	0.61	0.65	69	*sec*-butylbenzene	0.25	0.17
31	2-hexene (cis and trans)	0.33	0.27	70	*n*-decane	0.00	0.00
32	methylcyclopentane/3-methyl-*trans*-2-pentene	1.17	0.77	71	1,2,3-trimethylbenzene	1.21	1.26
				72	indane	0.62	0.66
33	2,4-dimethylpentane	1.15	0.86	73	isobutylbenzene	0.42	0.48
34	methylcyclopentene	0.00	0.00	74	1-methyl-3-*n*-propylbenzene	1.15	1.32
35	benzene/cyclohexane	1.76	1.96	75	1,3-diethylbenzene	0.67	0.78
36	cyclohexene/2,3-dimethylpentane/2-methylhexane	2.73	1.31	76	1-methyl-3-isopropylbenzene	0.82	0.99
				77	1,2-diethylbenzene	0.57	0.68
37	3-methylhexane	1.91	1.04	78	2-methyldecane	1.83	1.38
38	2,2,4-trimethylpentane	3.75	2.07	79	C_{10} aromatic	1.53	1.62
39	*n*-heptane	1.23	0.42	80	C_{10} aromatic	0.51	0.67
40	methylcyclohexane	1.57	0.33	81	*n*-undecane	0.75	0.69
41	dimethylhexene	0.28	0.25	82	C_{10} aromatic	0.77	1.03
42	2,2-dimethylhexane	0.12	0.18	83	unknowns	7.90	10.17
43	2,4- and 2,5-dimethylhexane	1.14	0.84				
44	2,3,4-trimethylpentane	0.00	0.00		percent aromatics	31.23	44.20
45	2,3,3-trimethylpentane	2.26	1.82		percent olefins	10.54	9.33
46	toluene/2,3-dimethylhexane	5.54	20.25		percent paraffins	58.23	46.47

[a] Same numbering scheme as used in the supplementary material.

4.9% to 9.6% of the total. The higher octane fuel showed a higher aromatic content of 45% over 32% for the regular-grade fuel. This increase was due to an increase in toluene from 5.5% to 20.2%. The benzene content of both fuels was very similar, 1.76% and 1.96%. The premium fuel was only used for cars 1–6. All others were tested on the regular-grade fuel. The switch was not intended but was required due to an inventory error.

Test Facilities. Road load and inertia simulation were achieved with a Horiba Model CDC800/DMA 915 computerized dynamometer. This is a dc electric dynamometer. The vehicle exhaust was directed into an 18-in. stainless steel dilution tunnel connected to a positive displacement pump, constant volume sampling system (CVS). This system provided all the gas-phase samples except for aldehydes, which were sampled via a heated probe directly from the tunnel. Hot soak evaporative emissions were collected from a "sealed housing for evaporative determination" (SHED). A more detailed description of the facilities has been given (*4*, *5*).

Test Procedures. To simulate as wide a range of driving conditions as was practical, three test cycles were utilized during this program. The standard FTP (*10*) (19.56 mph average speed) was used except for the diurnal evaporative portion. This portion was not used due to difficulty in preparing the wide variety of vehicles with appropriate instrumentation and heat blankets. The three test phases (bags) were analyzed separately and then combined by the standard calculation into the data presented here. The NYCC (7.07 mph average speed) was chosen as a typical low-speed cycle to represent city driving. The CUE or sulfate cycle (34.79 mph average speed) was chosen to represent normal high-speed driving, with the FTP representing normal urban driving.

After acquisition, each vehicle received an initial visual inspection to assure that all control systems were present and connected. One vehicle (no. 35) did not have the belt on the air pump, and another (no. 12) appeared to have been operated on leaded fuel. They were tested "as received" and were indistinguishable from other vehicles of the same year.

The fuel tank was then siphoned dry, and the vehicle was driven about 0.5 mi to the fuel storage facility. No vehicle ran out of fuel on this trip. The vehicle was filled with test fuel and driven to the weigh station where actual vehicle weight was recorded. On return (about 30–40 mi of driving), it was prepared or the next day's run by running an FTP cycle; EPA test protocol was followed throughout, with the omission of the diurnal evaporative cycle. A cold-start FTP cycle was run, followed by the hot soak evaporative test. This was followed by the CUE and NYC cycles.

Routine analyses was made to determine total hydrocarbons by flame ionization (FID); carbon monoxide and carbon dioxide were analyzed by nondispersive infrared; the oxides of nitrogen were determined by chemiluminscence. The FID instrument used for the CVS bag analysis was unheated, but the instrument used on the SHED was a heated version. Routine measurements were made of all operating parameters.

Detailed hydrocarbon analysis was performed on a bag sample taken directly from the CVS bag or directly from the SHED. All bags were made of Tedlar, a registered trademark of Du Pont. The detailed gas chromatographic (GC) analysis was accomplished on a multicolumn system comprised of a dual-bed $^1/_8$-in. o.d. packed column of Porapak QS (75% Q, 25% S), followed by silica gel column to separate the methane and the two-carbon hydrocarbons and by an F50 Versilube WCOT stainless steel capillary column to separate the three-carbon and higher hydrocarbons. The packed column was maintained at ambient temperature, approximately 25 °C. The capillary column was programmed from −45 to 85 °C at 8 deg/min after the initial injection at −95 °C. A single FID sensed both columns. The system has been described in detail (*11*). Approximately 150 individual hydrocarbons can be separated with this method, of which 82 have been identified here. The rest were grouped as unknowns. Identification was by relative retention time and boiling point and was confirmed with known compounds where possible.

Aldehyde analysis was accomplished by sampling in parallel with the CVS, during the time that each bag was collected, through a chilled bubbler containing acidified dinitrophenylhydrazine (DNPH) in acetonitrile. An aliquot of this solution was analyzed by reversed-phase gradient programming of two 25 cm × 4.6 mm i.d. Zorbax ODS columns in series from 60% to 100% acetonitrile in water. A visible detector set at 360 nm was used. Standards of known aldehyde derivatives were used for daily calibration. Acetone and other ketones that may have been present were identified by this system and reported whenever detected. They were not included in the total aldehyde summation. A more complete discussion of the technique has been given (*9*, *12*).

System Repeatability. To assure that all of the equipment was functioning correctly as a system, approximately every fifth vehicle was tested in duplicate. This was done in addition to all of the other normal calibrations and systems checks. This meant that 10 of the vehicles were tested in duplicate. Overall, repeatability was considered quite good, but the vehicle to vehicle spread was quite large. Generally, the worst case was the vehicle initially tested, which was tested 6 times, 4 times with full, detailed data. The standard deviation of the worst case vehicle was more than 5 times the average deviation of the other nine vehicles for all regulated pollutants and fuel economy. The average standard deviation of the nine best replicated vehicles was about 5% for the regulated emissions and 1.4% for fuel economy. The average standard deviation of individual hydrocarbons from both the hot soak and the exhaust emissions depended on the concentration and nature of the compound and its source. For abundant species that were reasonably separated, the standard deviation was less than 15% of the individual mass present and less than 10% on a compositional basis.

All data manipulations and transfers have been verified; each individual point was checked at all major interfaces.

Results and Discussion

All data from multiple runs on a single vehicle were averaged. The average regulated emissions by model year are reported in Table III. The complete data by individual vehicle, averaged for duplicate runs, with identification, control technology used, fuel, and speciation for both aldehydes and hydrocarbons are available in the supplementary material. All ratios used throughout this paper were calculated from the original run data and then averaged. All of the comparisons and other interpretations were made on the averaged data to prevent excessive weighting of those vehicles that were tested more than once.

A cursory comparison was made of the vehicles' regulated emissions according to model year. No attempt was made to correct for possible waivers or deterioration, especially in 1981. Eight vehicles, or 17%, passed all three exhaust emissions standards, 37% and 39% passed the carbon monoxide and hydrocarbon standards, respectively, and 63% passed the oxides of nitrogen standard. Because a full evaporative sequence was not run, the comparison with the evaporative standard is fallacious. If the diurnal test values were as high as the hot soak test values, 54% of the 1978 and later model vehicles would have passed.

Regulated Emissions. Table III shows several trends. As expected, fuel economy in miles per gallon improved with the higher speed cycles: NYCC < FTP < CUE, for

Table III. Regulated Emissions by Model Year[a]

year	CO			detailed HC			HS	NO_x			mpg		
	NYCC	FTP	CUE	NYCC	FTP	CUE	evap[b]	NYCC	FTP	CUE	NYCC	FTP	CUE
1975	92.1	32.2	19.3	13.8	4.58	2.62	11.6	3.42	2.28	3.38	9.2	18.0	20.4
1976	56.2	20.3	9.7	6.80	2.13	1.04	14.0	5.44	3.65	9.75	8.4	16.4	21.0
1977	87.3	29.0	22.8	13.0	3.35	2.06	15.3	5.19	3.37	3.63	11.7	22.7	28.7
1978	67.8	26.0	22.5	7.91	2.98	1.94	4.4	5.19	3.90	4.24	9.6	18.6	22.7
1979	55.0	20.8	15.4	8.53	2.18	1.34	3.5	4.36	2.88	3.15	10.9	21.0	26.8
1980	33.7	13.7	12.2	2.89	1.34	0.81	4.2	2.45	1.61	2.11	9.9	20.9	23.2
1981	29.1	8.38	9.03	2.95	0.77	0.49	1.1	2.09	1.32	1.23	12.6	23.9	28.4
1982	18.6	4.28	5.84	2.54	0.57	0.31	2.5	1.49	0.83	0.80	10.7	20.4	25.5
all	46.9	16.3	13.1	6.12	1.80	1.08	5.6	3.30	2.18	2.43	10.8	21.1	25.4

[a] All data is in grams per mile, except for the HS evap. [b] HS evap, hot soak evaporative emissions, grams per test.

all years. The overall average fuel economy by model year appeared to increase, but the increase was small enough and variable enough to not be considered statistically significant.

The oxides of nitrogen did not show any apparent decrease until 1980, when the standards were tightened. Hydrocarbons and carbon monoxide decreased linearly with decreasing age for all cycles with a correlation coefficient of between 0.86 and 0.99 if the four 1976 vehicles were excluded. The values seen for these four vehicles were highly variable with three unusually low on all cycles. No explanation for these results is apparent. The slope of the decrease was dependent upon cycle speed and pollutant, NYCC > FTP > CUE; for hydrocarbons the slopes were 1.9, 0.6, and 0.4 g/year, respectively, while for carbon monoxide the values were 11.7, 4.3, and 2.4 g/year.

Attempts were made to correlate the various regulated emissions and fuel economy (carbon dioxide). There were no consistent patterns within the 46-car data set. The closest to being correlated were CO and the hydrocarbons, but this was still poor to fair, with much scatter. This pattern was true for all bags and cycles. Overall, no pattern emerged, and no strong relationship between pollutants emerged.

Total Hydrocarbon. In this study, total hydrocarbon measurements were made by two different analytical techniques. The first was by the classic FID with its premixed flame. An unheated model was used for analysis of the CVS bags of exhaust emissions, and a heated version was used to monitor the SHED for the hot soak evaporative emissions test. The second technique was the GC analysis of the detailed hydrocarbons. The summation of the results of this analysis in grams per mile, which was calculated for each compound, provides a measurement of total hydrocarbon. This technique uses flame ionization for detection, but the flame is a diffusion type and the matrix is constant and known, helium. There are minor differences in response for each hydrocarbon in each system when compared to propane. There are also potential matrix problems due to the presence of oxygen in the FID (*13*, *14*). The summation of the GC speciation may not reflect the presence of compounds with high molecular weight (above C_{11}), resulting in a low total hydrocarbon quantitation. The summation of all of the potential errors should be less than 10% in the worst case.

In this study, a constant bias was seen in which the FID determined 77% with a standard deviation of 11% of the exhaust hydrocarbon as seen by the GC. The differences between cycles were insignificant, and the consistency was good. This large a difference was not seen in the SHED data with the hot FID, which averaged over 90% of the GC sum. The FIDs and GCs were cross-calibrated and checked with National Bureau of Standards standard mixtures of propane throughout the study and gave identical readings. There was no bias due to the concentration. Comparison of the 77% seen on the FTP cycle, for example, with the expected value of 100 yielded a Student's t value of 20.55. The upper limit of this ratio at the 99.99% confidence level is 81.9. The NYCC and CUE yielded similar results. The hot soak test had a value of 92.4, which was significantly below 100 at the 98% confidence level. The hot soak test data had three extreme values, two high and one low. The difference of 7.6% can be explained as the summation of the response errors previously mentioned. A few exploratory cross-calibrations with aromatics, using both the cold FID and the GC on the same bag, indicated that the response of the FID decreased as the molecular weight increased. This result was not quantitated but could be the result of surface absorption in the capillary to the FID. Because both systems analyzed exhaust and calibration samples from the same bags, system losses were ruled out as a source of error. In this study, there were more higher molecular weight hydrocarbons reported than had been seen previously. It is felt that these may be the cause of the bias and that the actual hydrocarbon concentrations reported by the FID were at least 23% lower than the actual values. The individual data points were normally distributed about this value.

Hydrocarbon Speciation Relationships and Trends. A total of 82 individual hydrocarbon species were analyzed. It was not practial to examine all possible relationships and interactions. The sums of the paraffins, olefins, and aromatics were created and examined, in addition to several other compounds of direct and indirect importance. The representativeness of the sums chosen was also briefly tested.

Overall, one of the more surprising findings was the consistency in composition of the sums and in some of the more abundant species. There was little difference between the consistency of the whole data set calculated as the percent of total and that calculated on a non-methane basis. Emission composition of the 46 vehicles had the most variability in the CUE cycle. The FTP and the NYCC gave similar results, but the variability was less for the NYCC. The average percent standard deviation for the NYCC was 66%, for the FTP was 68%, and for the CUE was 97%. The higher deviations in the CUE data may have been due to the lower concentrations seen. Generally, those compounds with the large standard deviations were the least abundant and accounted for less than 1% of the total. Acetylene was highly variable, as expected, as catalysts selectively reduce the amount present. This reduction leads to large variability when the whole data set is examined. This variability extends to individual olefins as well, but the sum of the olefins was

remarkably consistent. The individual compounds were summed into paraffins, olefins, and aromatics, with the results shown in Table IV. The percent standard deviations are even more surprising because of the use of two fuels of grossly different composition, as well as the degree of control-device effectiveness. These standard deviations (S) are the values for the individual data sets and are not those of the mean. To obtain the value for the mean, the S value should be divided by 6.7 ($45^{1/2}$).

For the individual species, 47 had S values below 50% on the NYCC and below 50% on the FTP. Only 8 and 11, respectively, had percent deviations greater than 100%. This consistency is somewhat at odds with the breakdown by model year, which showed several specific trends that might have been reflected in higher variability. Some of these data are shown in Table IV for all cycles and hot soak emissions. Methane, for example, was relatively constant through 1979 and then increased linearly from an average value of 7.8% of the total hydrocarbons to almost 25% of the total in 1982. This represents 5.6% per year. Acetylene showed an opposite pattern. Two years, 1975 and 1977, showed high values, which were probably due to rich operation and poorly functioning catalysts. If these years are included, the average from 1975 to 1979 is 3.6%; if not, it is 2.3%. Specifically in 1977, there was one vehicle with 14.6% acetylene, and the rest were below 6%. The CO for the same vehicle measured 71 g/mi for the FTP. For this vehicle, the same values were higher in all three bags, with bag 2 being the highest of the three. Overall, from 1979 to 1982, the percent acetylene of the total hydrocarbon decreased to 0.5%, with the largest decrease being between 1981 and 1982.

The olefins showed a step decrease between 1980 and 1981, from about 23% to 15%, with no other pattern discernible. The aromatics dropped from an average of 26% in 1975–1979 to 19% in 1980–1981 and then to 16% in 1982. The percentage of paraffins increased slightly more rapidly than that of methane, from 48% to 70% of the total.

The fuel difference could be seen in the percent of specific fuel components that had large differences, such as toluene, and in the percent total aromatics. The total olefins showed no differences, and the paraffin data strongly overlapped when the vehicles operated on each fuel were compared.

The utility of the sums was checked against the variations of an individual component of the sum by regression analysis for each vehicle. Benzene, toluene, and m- and p-xylene were individually associated to the total mass of aromatics. Methane, isobutane, n-butane, and isopentane were associated to the total mass of paraffins. Ethylene, propylene, and the C_4 olefins were associated to the total mass of olefins. The totals correlated reasonably well with the individual components on a mass basis, with R^2 values greater than 0.8 in most cases. The olefins that were combustion products generally had the strongest correlation: $R^2 > 0.9$. The 19 individual components shown in Table IV accounted for 55%–70% of the total hydrocarbon seen.

Benzene. A species of major current interest is benzene. In this study, benzene was not resolved from cyclohexane, and the two are reported together. It is estimated that 50% of the amount stated is benzene. The two fuels used in this program had similar levels of benzene: 1.76% and 1.96%, respectively. The results are summarized by cycle and model year and for evaporative emissions in Table V. Although exhaust emissions decreased markedly after 1979, the composition remained constant. Evaporative emissions decreased each year through 1981 and then leveled off (actually rose slightly). The percentage of benzene plus cyclohexane in the exhaust increased with an increased average speed, from 2.7% for the NYCC to 4.1% for the CUE. The percent standard deviation also increased with speed from 39% to 50%.

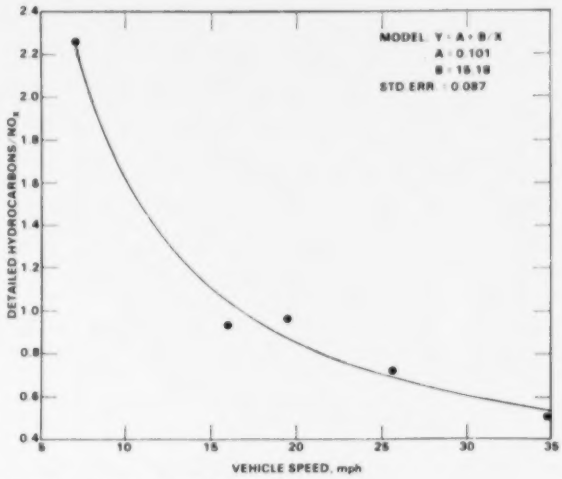

Figure 1. Average HC/NO_x ratio by weight.

Hydrocarbon to NO_x Ratio. The amount of hydrocarbon in relation to the amount of oxides of nitrogen present is rate determining in the production of photochemical smog. As this ratio decreases, the immediate potential to produce ozone decreases. The oxide of nitrogen that is initially emitted from automobiles is predominately nitric oxide, which must be converted to nitrogen dioxide before the reaction leading to stable ozone formation can begin. Nitric oxide will preferentially react with ozone, effectively preventing it from persisting until the nitric oxide is at minimum levels.

In this study, each cycle represented a separate average speed. A comparison of emissions by average speed generally indicates that as the average speed increases, emissions on a per mile basis decrease. This decrease would be a trend at best and not statistically significant if the NYCC were not included. Ignoring bag 1 of the FTP because of its cold start, all other data points were included. Results from bag 2 were generally lower than might be expected, probably due to the absence of a start that occurred in all other cycles and to the fact that the catalyst was operating at its optimum efficiency. This trend was typical for all emissions including NO_x, although the increase at low speeds was much less pronounced. It followed for all model years when examined separately.

When the ratio of hydrocarbons to oxides of nitrogen on a gram per mile basis was determined, it showed a similar pattern to that shown by the individual emissions, but one that was smoother and did not show as much discontinuity in bag 2. This ratio for both summed GC hydrocarbons and the FID are shown in Table VI. This curve (Figure 1) was best modeled by a reciprocal relationship, $y = A + B/X$, where y = ratio HC/NC, X = average speed, $A = 0.101$, and $B = 15.18$, from the detailed hydrocarbon data. The most interesting feature of this curve is that the values for the NYCC are in the range at which atmospheric reaction of HC and NO_x will proceed without additional reactants. Most current emission models such as Mobile 2 and AP-42 (*15*) are based on a more nearly linear relationship of speed with the FTP data. Most surveillance data report FTP data only. This study

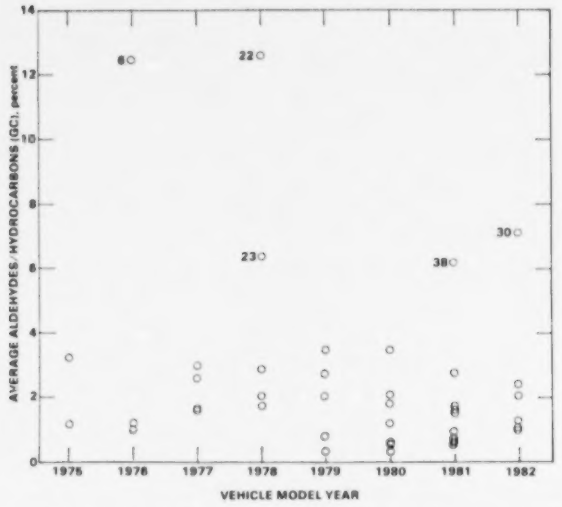

Figure 2. Scatter plot of percent of aldehydes by model year. Numbers next to data points refer to vehicle number as listed in the supplementary material.

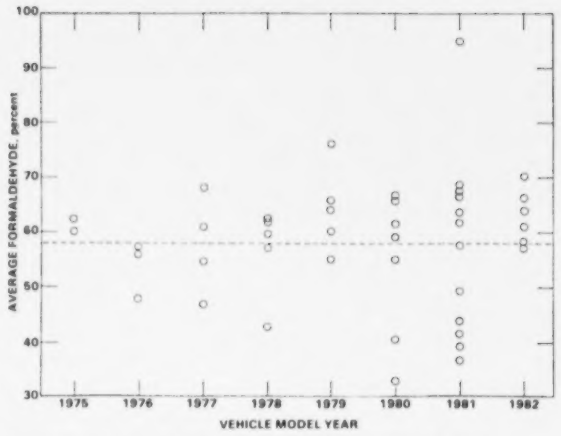

Figure 3. Scatter plot of percent of formaldehyde by year.

has the potential of providing a unique insight into the actual automotive contribution to smog formation by utilizing variable-speed driving patterns with different average speeds to define emission patterns. If this curve can be extrapolated to even slower speeds, as would be seen in highly congested center-city areas, the mixture would be even more rapidly reactive. This could indicate that, at low speeds, the first day ozone formation observed could be a local phenomenon and additional hydrocarbons from other sources would only serve to increase the rate of ozone formation.

Aldehydes. Aldehyde measurements were made on all but one of the runs. The percentage of total hydrocarbons that were aldehydes was fairly constant. Figure 2 is a scatter plot of the FTP data by model year. The data are shown in Table VII along with the percentage of total aldehydes that is formaldehyde, acetaldehyde, and benzaldehyde. On inspection, Table VII would seem to indicate that the percentage of aldehydes decreased in 1981 and 1982. Examination of Figure 2 indicates that three vehicles with very high emissions dominate the 1976 and 1978 emissions and that the lowest values were seen in 1979 and 1980. Only five values exceeded 4% and those vehicles are labeled. The labels shown in Figure 2 are identifying numbers of the individual vehicles (used in the supplementary material). The use of non-methane hydrocarbons as a base changes the values by about 10%, but the patterns are the same. The percentage of aldehydes appeared to increase slightly from 2% to 3% with increasing cycle speed. The means of the NYCC and CUE overlap at two standard deviations.

The percentage ot total aldehydes that is formaldehyde showed remarkable consistency at about 60% of the total aldehydes. In general, the scatter easily encompassed the mean, and no trends were seen (Figure 3). Acetaldehyde appeared to be more abundant particularly in 1981 and 1982, and benzaldehyde was less abundant. This trend is consistent with increased catalytic activity, favoring reduction of higher molecular weight species.

Comparison with Previous Studies. The bulk of previous work only described regulated emissions from automobiles. However, there has been continuous interest in detailed analyses of the hydrocarbons emitted and the associated aldehydes. Among other studies, Jackson (*6*) reported on 34 cars in 1978, and Black and High (*4*) reported on 22 cars in 1977. These studies were chosen to be illustrative of past studies and are among the most recent work that included more than a few vehicles. The vehicles in these studies were new, i.e., low mileage, or prototype vehicles, and all were tuned to the manufacturers' specifications. In this study, all vehicles were tested as received, after visual inspection. It should be remembered that all of these studies used different fuels, which might bias distributions. All reported on the FTP cycle.

A comparison of selected runs and components is possible. The data were presented as percent of total hydrocarbon. In the two earlier studies, the vehicles before 1975 did not have catalysts. In the Black and High study, the cars without catalysts were primarily lean burn controlled. The catalyst impact is seen in a dramatic, though erratic, increase in the paraffins (primarily methane) and a corresponding decrease in olefins and the specific emissions of ethylene, acetylene, and benzene. In this study, in which all of the cars were equipped with catalysts, a similar pattern was seen after 1980.

If it is to be assumed that the older cars were similar to the nonconverter case (i.e., there was deterioration of the catalyst), a comparison of the impact of catalysts may be made. The studies are in good agreement on the impact of the catalyst on the total olefins (32%–41% reduction), ethylene (41%–50% reduction), and acetylene (61%–74% reduction), which are all combustion products and chemically reactive species. This study showed the largest impact on aromatics (28% vs. 8% and 18% reduction) but the least impact on benzene, which showed no change (vs. a 50%–26% reduction). The Jackson study showed the maximum increase in paraffins to be 69% compared to 40% and 38% in the two other studies.

An earlier study of Bonamassa and Wong Woo (*16*) can also be used for comparison, particularly on the average overall composition as a general indication of changes since the advent of catalysts. In Table VIII, unweighted averages are presented on both a total hydrocarbon and a non-methane hydrocarbon basis, which is the basis of the study done by Bonamassa.

The fuels had generally similar compositions of total paraffins, olefins, and aromatics in all studies except that of Jackson, in which composition was not given. Values for methane agreed well for the three more recent studies, and its value was unknown in the Bonamassa study. Values for acetylene agreed between this study and that of Jackson at about half the level seen by Black and High and Bonamassa and Wong Woo. Overall this study agreed

Table IV. Hydrocarbon Composition of Exhaust and Evaporative Emissions, Weight Percent of Total Hydrocarbon (GC)

	1975	1976	1977	1978	1979	1980	1981	1982	average[a]
(A) Exhaust Emissions (FTP Test)									
paraffins									
methane	7.2	9.3	8.8	8.1	7.2	13.5	19.7	23.8	13.9 ± 8.0
isobutane	0.5	0.7	0.6	0.7	0.5	0.6	0.9	0.7	0.7 ± 0.3
n-butane	4.9	4.6	4.5	3.8	3.7	4.7	5.7	5.1	4.8 ± 1.6
isopentane	3.6	4.0	3.0	3.3	3.3	3.4	4.4	3.4	3.7 ± 1.2
n-pentane	1.7	1.8	1.5	1.7	1.4	1.6	1.8	1.9	1.7 ± 0.5
3-methylpentane	1.0	1.1	0.8	1.0	0.9	0.9	1.1	1.4	1.0 ± 0.4
2,2,4-trimethylpentane	2.3	2.4	2.4	1.9	2.0	2.1	2.4	2.4	2.2 ± 0.7
total paraffins	45.8	48.7	47.5	43.8	46.5	53.7	63.1	69.4	54.8 ± 11.3
olefins									
ethylene	9.2	10.2	7.7	10.1	8.1	9.8	5.9	3.6	7.6 ± 3.9
propylene/propane	3.4	3.6	2.9	4.2	3.1	3.9	1.8	1.2	2.6 ± 1.7
butenes	2.1	2.7	2.1	4.0	2.4	2.4	1.4	1.0	2.1 ± 1.1
pentenes	1.7	1.7	2.2	1.6	1.5	1.6	1.1	1.0	1.5 ± 0.6
hexenes	1.0	0.8	0.8	0.9	0.9	0.8	0.5	0.6	0.7 ± 0.3
total olefins	21.0	22.2	19.4	24.4	19.6	21.2	14.6	11.6	18.3 ± 6.4
acetylene	5.2	2.1	6.6	2.7	2.1	2.0	1.3	0.5	2.3 ± 2.5
aromatics									
benzene/cyclohexane	2.7	3.6	2.6	3.4	3.8	3.0	3.2	3.2	3.2 ± 1.3
toluene/2,3-dimethylhexane	5.5	7.6	5.2	9.1	9.2	4.7	4.3	3.3	5.8 ± 3.7
ethylbenzene	1.0	0.9	1.0	1.0	1.1	0.8	0.7	0.7	0.9 ± 0.3
p- and *m*-xylene	3.6	2.8	3.5	2.6	3.5	2.9	2.2	1.8	2.7 ± 0.9
o-xylene/C_9 paraffin	2.2	1.5	2.2	1.6	2.1	1.8	1.8	1.4	1.8 ± 0.6
1,3,5-trimethylbenzene	2.7	2.2	2.2	2.4	2.5	2.0	1.9	1.3	2.1 ± 0.7
total aromatics	27.7	26.7	26.2	28.8	31.6	23.0	21.0	18.5	24.5 ± 6.2
(B) Evaporative Emissions (Hot Soak Test)									
paraffins									
isobutane	4.3	6.8	4.9	2.3	3.7	6.8	5.3	2.6	4.8 ± 4.5
n-butane	29.2	33.5	34.1	15.8	17.5	16.9	19.3	19.2	23.2 ± 14.9
isopentane	16.5	15.3	16.4	13.6	10.7	9.7	6.4	10.9	10.9 ± 5.2
n-pentane	7.1	5.2	6.4	5.0	4.0	3.9	3.2	4.7	4.4 ± 1.9
3-methylpentane	2.1	1.0	1.6	2.2	1.6	1.3	1.0	1.2	1.4 ± 0.7
2,2,4-trimethylpentane	1.9	1.8	1.4	1.5	1.8	1.3	1.7	2.0	1.7 ± 0.8
total paraffins	73.6	73.1	72.7	59.2	59.3	63.9	56.4	61.8	62.8 ± 10.0
olefins									
propylene/propane	0.6	1.0	0.8	0.6	4.0	1.2	1.9	0.5	1.6 ± 2.5
butenes	2.8	3.1	3.4	2.1	2.0	4.3	1.7	1.8	2.6 ± 2.3
pentenes	6.4	4.9	5.7	5.4	4.1	3.4	3.3	4.6	4.3 ± 1.6
hexenes	2.1	1.8	1.5	2.4	1.6	2.9	2.7	2.0	1.8 ± 0.7
total olefins	19.6	19.2	20.2	15.6	17.8	18.5	15.2	15.4	17.2 ± 3.9
aromatics									
benzene/cyclohexane	1.3	1.1	1.0	1.8	1.1	1.2	2.1	1.8	1.5 ± 0.9
toluene/2,3-dimethylhexane	2.2	3.0	2.2	9.9	6.9	5.3	8.6	6.6	6.3 ± 5.0
ethylbenzene	0.2	0.2	0.2	0.7	0.8	0.6	1.0	0.9	0.7 ± 0.5
p- and *m*-xylene	0.8	0.7	0.9	2.3	2.7	2.3	3.8	3.4	2.5 ± 1.7
o-xylene/C_9 paraffin	0.5	0.4	0.5	1.2	1.4	1.2	1.8	1.9	1.3 ± 0.9
1,3,5-trimethylbenzene	0.4	0.5	0.5	2.2	1.7	1.3	2.0	1.9	1.5 ± 1.2
total aromatics	6.8	7.7	7.1	25.2	22.8	17.6	28.3	22.7	20.0 ± 12.9
(C) Exhaust Emissions (NYC Test)									
paraffins									
methane	6.1	6.6	7.3	5.6	5.5	10.4	10.0	14.0	8.8 ± 6.1
isobutane	0.5	0.9	0.4	0.7	0.5	0.6	0.8	1.1	0.7 ± 0.4
n-butane	3.9	4.9	3.7	3.6	3.8	4.6	6.1	6.4	4.9 ± 2.0
isopentane	2.5	4.2	2.8	4.5	3.1	3.5	4.7	4.4	3.9 ± 1.5
n-pentane	1.2	1.6	1.5	1.8	1.3	1.7	2.0	2.2	1.7 ± 0.7
3-methylpentane	0.7	1.0	0.7	0.9	0.5	0.7	0.8	1.3	0.8 ± 0.4
2,2,4-trimethylpentane	1.7	2.1	1.9	1.8	1.7	1.9	2.2	2.4	2.0 ± 0.6
total paraffins	43.6	47.1	44.4	42.1	45.1	50.7	55.4	62.7	50.5 ± 9.0
olefins									
ethylene	8.3	10.3	8.8	8.7	7.6	8.8	6.9	4.7	7.7 ± 3.4
propylene/propane	3.0	3.8	3.1	3.5	2.5	1.6	1.2	1.9	2.2 ± 1.4
butenes	1.8	2.9	2.4	3.0	2.2	2.4	1.9	1.7	2.2 ± 1.0
pentenes	1.4	1.9	1.6	1.9	1.5	1.6	1.3	0.9	1.5 ± 0.5
hexenes	0.7	1.0	0.8	1.2	0.9	1.0	0.8	0.8	0.9 ± 0.4
total olefins	19.8	21.2	20.7	21.3	18.9	19.3	16.5	15.2	18.5 ± 5.4
acetylene	4.6	1.1	5.4	1.9	1.9	1.4	0.8	0.0	1.7 ± 3.0
aromatics									
benzene/cyclohexane	2.4	2.9	2.5	2.5	3.1	2.3	2.9	2.3	2.7 ± 1.0
toluene/2,3-dimethylhexane	5.5	7.6	5.3	10.8	8.8	4.4	5.3	3.1	6.1 ± 3.8
ethylbenzene	1.0	1.0	1.0	1.2	1.2	1.0	0.9	0.8	1.0 ± 0.2
p- and *m*-xylene	4.0	3.2	3.7	3.3	3.6	3.4	3.0	2.0	3.2 ± 0.9
o-xylene/C_9 paraffin	2.4	1.8	2.3	1.9	2.0	2.0	1.9	1.4	1.9 ± 0.5
1,3,5-trimethylbenzene	2.7	2.4	2.6	3.3	2.9	2.8	2.4	1.8	2.6 ± 0.8
total aromatics	31.7	30.3	29.4	34.5	33.9	28.5	27.2	22.1	29.1 ± 5.9

Table IV (Continued)

	1975	1976	1977	1978	1979	1980	1981	1982	average[a]
				(D) Exhaust Emissions (CUE Test)					
paraffins									
methane	7.0	10.4	8.0	10.0	7.3	15.8	23.0	34.7	16.6 ± 11.4
isobutane	0.6	0.8	0.6	1.0	0.5	0.6	0.8	0.7	0.7 ± 0.4
n-butane	4.8	4.8	4.4	3.6	4.1	5.6	5.6	4.9	4.9 ± 1.8
isopentane	3.3	4.2	3.3	4.3	3.1	4.0	4.3	3.4	3.8 ± 1.7
n-pentane	1.6	1.7	1.3	1.6	1.3	2.1	1.8	1.8	1.7 ± 0.8
3-methylpentane	0.8	1.1	0.7	0.8	0.6	0.9	1.0	1.2	0.9 ± 0.7
2,2,4-trimethylpentane	1.9	2.2	1.8	1.4	1.7	1.8	1.9	1.6	1.8 ± 0.9
total paraffins	44.8	49.4	44.8	45.3	47.5	57.5	66.5	74.0	56.8 ± 14.1
olefins									
ethylene	11.3	13.1	11.2	12.8	9.2	10.9	5.5	4.2	8.9 ± 5.7
propylene/propane	4.8	4.1	4.4	3.8	3.2	3.2	1.9	1.5	3.0 ± 1.8
butenes	2.7	2.9	2.8	3.1	2.4	2.4	1.4	0.9	2.1 ± 1.1
pentenes	1.7	1.9	1.5	1.8	1.4	1.1	0.8	0.3	1.2 ± 0.8
hexenes	0.9	0.8	0.7	0.6	0.8	0.5	0.2	0.1	0.5 ± 0.5
total olefins	25.2	25.8	24.7	25.0	21.2	22.4	14.0	10.9	19.5 ± 8.1
acetylene	2.4	2.3	3.9	3.2	1.8	1.4	0.6	0.0	1.6 ± 2.4
aromatics									
benzene/cyclohexane	3.3	4.0	3.7	4.6	4.2	3.8	4.0	5.1	4.1 ± 2.1
toluene/2,3-dimethylhexane	5.5	5.7	5.7	8.5	8.3	3.6	3.2	1.8	4.8 ± 3.7
ethylbenzene	0.9	0.6	0.9	1.0	1.1	0.7	0.5	0.3	0.7 ± 0.4
p- and *m*-xylene	3.5	2.0	3.4	2.4	3.1	2.2	1.5	0.7	2.1 ± 1.2
o-xylene/C_9 paraffin	2.2	1.3	2.2	1.1	1.6	1.4	1.1	0.6	1.4 ± 0.6
1,3,5-trimethylbenzene	2.3	1.4	2.0	1.8	1.9	2.2	1.4	1.5	1.8 ± 1.3
total aromatics	27.0	22.2	26.3	26.0	29.3	18.6	18.9	15.1	21.9 ± 7.0

[a] Linear average of all 46 cars ± 1 SD.

Table V. Average Benzene plus Cyclohexane Emissions

		cycle							
		FTP		CUE		NYC		evap	
year	no. of vehicles tested	mg/mi	% total HC	mg/mi	% total HC	mg/mi	% total HC	mg/test	% total HC
1975	3	116.2	2.7	87.6	3.3	322	2.4	158	1.3
1976	4	79.8	3.6	45.8	4.0	204	2.9	131	1.1
1977	4	94.6	2.6	73.5	3.7	364	2.5	125	1.0
1978	5	113.7	3.4	88.8	4.6	234	2.5	68	1.8
1979	5	81.4	3.8	57.9	4.2	237	3.1	46	1.1
1980	7	40.4	3.1	32.5	3.8	87	2.3	39	1.2
1981	12	24.4	3.2	19.8	4.0	83	2.9	20	2.2
1982	6	16.1	3.2	16.6	5.1	62	2.3	30[a]	1.8
avg	46	59.0	3.2	43.7	4.1	165.	2.7	60[b]	1.5

[a] Average of 5 vehicles. [b] Average of 45 vehicles.

Table VI. Ratio of Hydrocarbon to Oxides of Nitrogen by Weight, 46-Car Average ± 1 Standard Deviation[a]

cycle	average speed, mph (Km/mi)	FID	ratio by weight, hydrocarbons determined by summed GC
FTP (weighed)	19.56 (31.5)	0.74 ± 0.55	0.97 ± 0.71
FTP (bag 1)	25.60 (41.2)	1.31 ± 0.72	1.41 ± 0.90
FTP (bag 2)	16.04 (25.8)	0.68 ± 0.77	0.94 ± 1.02
FTP (bag 3)	25.60 (41.2)	0.57 ± 0.42	0.72 ± 0.51
CUE	34.79 (56.0)	0.41 ± 0.25	0.51 ± 0.30
NYC	7.07 (11.4)	1.75 ± 1.48	2.26 ± 1.78

[a] Standard error of mean = standard deviation/6.78, n = 46.

very closely with the Jackson study on all compounds that were compared. These two studies showed lower amounts of the combustion products ethylene and propylene than Black and High's study but more ethylene than Bonamassa and Woo's study. The difference in toluene composition was undoubtedly due to differences in fuel composition.

There is not as much work available on aldehyde emissions. Much previous work was done with other methods, primarily 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH), which was not as accurate as the DNPH methodology currently employed. MBTH suffers from an uncorrectable SO_2 interference and a bias against aromatic aldehydes. This interference and bias yields results that are on average 20%–40% lower than those of the DNPH method. Individual values vary over a much wider range. Therefore, the only values directly compared were those obtained by the use of DNPH. Two studies had data that could be compared. The Bureau of Mines (*6*) ran a study on uncontrolled vehicles, model years 1970–1973, and generated both MBTH and DNPH values. The latter were calculated by the 1972 method. Assuming minimal differences between the two vehicle test methods, aldehydes were 6.0% ± 3.0% of the hydrocarbons on a mass basis vs. 2.5% in this study. A total of 10 cars were tested in duplicate in the Bureau of Mines study, and the percent of aldehydes ranged from 2% to 13%, with absolute values ranging from 0.1 g/mi to 0.4 g/mi. No breakdown of composition was given.

A study of Exxon (*8*) reported aldehydes on a mole percent basis that could be converted to a mass percentage. In this study, acetone was reported separately and not included in the total aldehydes. For comparison purposes,

Table VII. Aldehydes Composition

model year	NYCC				FTP				CUE			
	ald[a]	form[b]	acet[c]	benz[d]	ald[a]	form[b]	acet[c]	benz[d]	ald[a]	form[b]	acet[c]	benz[d]
1975	2.17	51.6	18.6	11.8	2.23	60.7	16.5	9.3	3.08	59.5	16.9	9.6
1976	2.93	58.1	23.6	12.4	4.90	53.2	23.8	14.7	6.56	59.0	24.4	9.8
1977	2.06	54.5	22.4	9.6	2.25	57.3	19.5	10.8	2.99	54.1	26.0	8.6
1978	3.41	57.2	20.8	9.8	3.28	55.0	20.2	12.9	5.12	52.2	22.6	14.9
1979	2.02	61.7	21.0	5.8	3.69	63.4	22.6	5.3	3.17	52.5	27.4	12.2
1980	2.30	62.5	22.5	6.4	1.45	54.0	26.3	9.7	2.88	55.2	28.0	9.8
1981	1.07	66.6	27.4	1.3	1.56	57.6	29.5	3.1	0.94	57.2	30.6	5.4
1982	1.00	65.7	27.4	3.2	2.78	62.0	28.3	3.7	1.15	60.1	34.3	1.55
avg	1.89	61.9	24.0	5.8	2.45	57.9	25.2	7.2	2.71	56.1	27.9	8.3

[a] Percent aldehydes of total GC hydrocarbons. [b] Formaldehyde, percentage of total aldehydes. [c] Acetaldehyde, percentage of total aldehydes. [d] Benzaldehyde, percentage of total aldehydes.

Table VIII. Exhaust Hydrocarbon Composition, Comparison of FTP Cycle, Percent of Total Mass (Carbon)

	our study		Black and High (1977)[a]		Jackson (1978)[b]		Bonamassa and Wang Woo (1966)[c], non-methane
	total	non-methane	total	non-methane	total	non-methane	
methane	13.9		13.5		14.5		
acetylene	2.3	2.6	4.8	5.2	2.2	2.6	5.2
ethylene	7.6	8.7	10.4	12.0	7.4	8.7	5.1
propylene	2.6	3.0	5.6	6.5	2.9	3.4	3.6
n-butane	4.8	5.7	4.6	5.3	5.5	6.4	
isopentane	3.7	4.4	4.3	5.0	5.4	6.3	
benzene	3.2	3.8	3.2	3.7	3.4	4.0	3.2
toluene	5.8	6.6	11.5	13.3	5.8	6.8	7.4
paraffins	54.8	48.1	54.0	47.2	56.5	49.1	27.8
olefins	18.3	21.0	22.5	26.0	15.1	17.7	16.7
aromatics	24.5	28.2	18.7	21.6	26.2	30.6	50.3

[a] SAE 7701544, average of all (ref 4). [b] SAE 780624, average for converter cars (ref 5). [c] Division of Water, Air, and Waste Chemistry, 152nd National Meeting of the American Chemical Society, New York, 1966.

the average FTP data for all 46 cars was recalculated to include acetone (Table IX). It must be remembered that acetone is highly variable. The overall agreement of these values is considered good, and the differences, other than acetaldehyde, are not significant for the commonly found species. The comparison with a more recent study of only two cars (*11*), one a 1974 and one a 1981 model, also gave comparable results (Table IX).

Conclusions

Some conclusions resulting from this work include the following:

(1) Overall, the composition of exhaust hydrocarbons was consistent through 1979. Changes seen in the exhaust composition from 1980 to 1982 were not large enough to strongly affect the deviations seen in the total data set, particularly the sums of the values of paraffins, olefins, and aromatics. After 1979, the values of methane and the paraffins increased, and those for acetylene, the olefins, and the aromatics decreased as percent of total.

(2) The individual components correlated with their respective sum with an R^2 of >0.9 for the olefins and >0.8 for other components. The composition of benzene as a percent of total was constant for all years.

(3) The fact that the average overall composition seems fairly constant, i.e., standard deviation less than 50% of the value, while the composition was actually changing due to catalyst function would indicate that in any fleet of vehicles the composition should also be reasonably consistent.

(4) Products of combustion showed the greatest changes by year. Fuel-related components such as toluene showed variability with fuel composition along with the variability associated with the greater reduction of aromatics due to the catalyst.

Table IX. Comparison of Aldehyde Composition

	percent of total aldehydes + acetone	
	this study	Wigg (*8*)
formaldehyde	44	48.7
acetaldehyde	19	9.9
C_3 aldehydes + acetone	29	22.1
benzaldehyde	5.4	8.2
tolualdehyde	0	5.5

	percent of total aldehydes		
	this study	Lipari (*9*)	
		1974 cold start	1981 cold start
formaldehyde	57.9	55.8	55.8
acetaldehyde	25.2	22.7	18.2
acrolein	5.1	11.6	5.8
benzaldehyde	7.2	8.2	16.4

(5) Evaporative emissions were mostly related to fuel composition with the two butanes and isopentane making up about 50% of the emissions prior to the use of the "shed test" in 1978 and 30% after that test was introduced.

(6) The aldehydes were about 2.5% of the total hydrocarbons for all years. Formaldehyde was 60% of the total aldehydes.

(7) Average cycle speed showed an increase in emissions with a decrease in speed. The most dramatic increase was in the hydrocarbon to NO_x ratio, which had a reciprocal relationship to speed. At the low speeds seen in the NYCC, photochemical reactions may be possible without an additional source of hydrocarbon.

(8) The standard FID measurement of total hydrocarbons yielded results that accounted for only 77% of the hydrocarbons seen by GC. The use of a hot FID on the

SHED yielded 92% of the GC results. This difference is statistically highly significant and, at present, not fully understood. It may be the result of "hang up" of higher molecular weight aromatics in the regular FID.

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Supplementary Material Available

A detailed description of the 46 vehicles and their control systems, complete component data by individual vehicle, control technology used, fuel, and speciation for aldehydes and hydrocarbons (49 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, authors names, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $79.00 for photocopy ($81.00 foreign) or $10.00 for microfiche ($11.00 foreign), are required.

Registry No. Methane, 74-82-8; ethylene, 74-85-1; ethane, 74-84-0; acetylene, 74-86-2; propylene, 115-07-1; propane, 74-98-6; propadiene, 463-49-0; methylacetylene, 74-99-7; isobutane, 75-28-5; 1-butene, 106-98-9; isobutylene, 115-11-7; *n*-butane, 106-97-8; 1,3-butadiene, 106-99-0; *trans*-2-butene, 624-64-6; 2,2-dimethylpropane, 463-82-1; *cis*-2-butene, 590-18-1; 3-methyl-1-butene, 563-45-1; isopentane, 78-78-4; 1-pentene, 109-67-1; 2-butyne, 503-17-3; *n*-pentane, 109-66-0; 2-methyl-1,3-butadiene, 78-79-5; *trans*-2-pentene, 646-04-8; *cis*-2-pentene, 627-20-3; 2-methyl-2-butene, 513-35-9; 2,2-dimethylbutane, 75-83-2; cyclopentene, 142-29-0; cyclopentane, 287-92-3; 3-methyl-1-pentene, 760-20-3; 4-methyl-1-pentene, 691-37-2; 2,3-dimethylbutane, 79-29-8; 2-methylpentane, 107-83-5; 2,3-dimethyl-1-butene, 563-78-0; 3-methylpentane, 96-14-0; 1-hexene, 592-41-6; 2-ethyl-1-butene, 760-21-4; *n*-hexane, 110-54-3; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; 2-methyl-2-pentene, 625-27-4; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; methylcyclopentane, 96-37-7; *trans*-3-methyl-2-pentene, 616-12-6; 2,4-dimethylpentane, 108-08-7; methylcyclopentene, 27476-50-2; benzene, 71-43-2; cyclohexane, 110-82-7; cyclohexene, 110-83-8; 2,3-dimethylpentane, 565-59-3; 2-methylhexane, 591-76-4; 3-methylhexane, 589-34-4; 2,2,4-trimethylpentane, 540-84-1; *n*-heptane, 142-82-5; methylcyclohexane, 108-87-2; dimethylhexene, 78820-82-3; 2,2-dimethylhexane, 590-73-8; 2,4-dimethylhexane, 589-43-5; 2,3,4-trimethylpentane, 565-75-3; 2,3,3-trimethylpentane, 560-21-4; toluene, 108-88-3; 2,3-dimethylhexane, 584-94-1; 2-methylheptane, 592-27-8; 1-methylcyclohexene, 591-49-1; 4-methylheptane, 589-53-7; 3-methylheptane, 589-81-1; 2,2,5-trimethylhexane, 3522-94-9; *n*-octane, 111-65-9; 2,3,5-trimethylhexane, 1069-53-0; 2,4-dimethylheptane, 2213-23-2; 2,5-dimethylheptane, 2216-30-0; 3,5-dimethylheptane, 926-82-9; ethylbenzene, 100-41-4; 2,3-dimethylheptane, 3074-71-3; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; 2-methyloctane, 3221-61-2; 2,4,5-trimethylheptane, 20278-84-6; *o*-xylene, 95-47-6; 2,4-dimethyloctane, 4032-94-4; *n*-nonane, 111-84-2; decane, 124-18-5; *n*-propylbenzene, 103-65-1; 1,3,5-trimethylbenzene, 108-67-8; 3,4-dimethyloctane, 15869-92-8; 1-methyl-3-ethylbenzene, 620-14-4; 1-methyl-2-ethylbenzene 611-14-3; 1,2,4-trimethylbenzene, 95-63-6; *sec*-butylbenzene, 135-98-8; 1,2,3-trimethylbenzene, 526-73-8; indane, 496-11-7; isobutylbenzene, 538-93-2; 1-methyl-3-propylbenzene, 1074-43-7; 1,3-diethylbenzene, 141-93-5; 1-methyl-3-isopropylbenzene, 535-77-3; 1,2-diethylbenzene, 135-01-3; 2-methyldecane, 6975-98-0; *n*-undecane, 1120-21-4; formaldehyde, 50-00-0; acetaldehyde, 75-07-0; acrolein, 107-02-8; acetone, 67-64-1; propionaldehyde, 123-38-6; butyraldehyde, 123-72-8; crotonaldehyde, 4170-30-3; benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0; hexanaldehyde, 66-25-1; 1-butyne, 107-00-6; 2,5-dimethylhexane, 592-13-2.

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